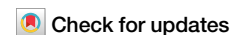


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Local structure of amorphous sulfur in carbon–sulfur composites for all-solid-state lithium–sulfur batteries



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All-solid-state (ASS) batteries are a promising solution to achieve carbon neutrality. ASS lithium–sulfur (Li–S) batteries stand out due to their improved safety, achieved by replacing organic solvents, which are prone to leakage and fire, with solid electrolytes. In addition, these batteries offer the benefits of higher capacity and the absence of rare metals. However, the low electronic conductivity of sulfur poses a major challenge for ASS Li–S batteries. To address this challenge, sulfur is often combined with porous carbon. Despite this standard practice, the local structure of sulfur in these composites remains unclear. Based on small-angle X-ray scattering and pair distribution function analysis, we discovered that sulfur in carbon–sulfur composites formed via melt diffusion is amorphous and primarily comprises S₈ ring-shaped structures. The carbon–sulfur composite demonstrated a high specific capacity of 1625 mAh g^{−1} (97% of the theoretical specific capacity of sulfur). This remarkable performance is attributed to the extensive contact area between carbon and sulfur, which results in an excellent interface formed through melt diffusion. The insights gained into the local structure of sulfur and the analytical approaches employed enhanced our understanding of electrochemical reactions in ASS Li–S batteries, thereby aiding in the optimization of material design.

Further development of rechargeable batteries for efficient energy use is crucial for achieving carbon neutrality. Applications such as electric vehicles, stationary energy storage systems, drones, and high-altitude pseudo-satellites require batteries with high safety, large capacity, lightweight construction, and high power output¹. The advancement of lithium-ion batteries can be credited to the pioneering work of Whittingham et al., who used TiS₂ as an intercalation electrode material², Goodenough et al.³, who explored a high-capacity layered oxide (LiCoO₂) as a cathode material, and Yoshino et al.⁴, who demonstrated the use of carbon as a safe and manageable anode material, leading to the practical implementation of lithium-ion batteries in 1991. Currently, the theoretical specific capacity of an anode based on graphite is 372 mAh g^{−1}^{5–7} while that of a cathode based on LiCoO₂ is relatively low (140 mAh g^{−1})^{3,8}. Consequently, extensive research efforts have focused on developing active cathode materials^{9–14}, aiming for specific capacities exceeding 300 mAh g^{−1}¹⁵.

Lithium–sulfur (Li–S)^{16–21}, lithium–air^{22,23}, all-solid-state (ASS)^{24–29}, sodium³⁰, and fluoride³¹ batteries have been studied as next-generation batteries. Silicon-based alloys with a maximum theoretical specific capacity of 4200 mAh g^{−1} are considered promising candidates for anodes^{32–38}. Meanwhile, the theoretical capacity of sulfur, which is the cathode material, is 1672 mAh g^{−1}^{16,17}. Therefore, developing positive electrode materials is crucial for next-generation batteries.

A major challenge in lithium-ion batteries is the use of organic solvents as electrolytes. Although these solvents offer excellent lithium-ion conductivity³⁹, they pose safety risks such as leakage and fire hazards and have a limited operating temperature range^{40,41}. In Li–S batteries, the performance is hindered by the dissolution of reaction intermediates, such as Li₂S_x (x = 2–8), into the solvent. This has shuttle effects, leading to capacity loss, cycle degradation, and increased resistance due to irreversible reactions¹⁸. ASS Li–S batteries can address these challenges. Solid-state

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Fig. 1 | Electrochemical evaluations of ASS Li-S cell. **a** Charge–discharge curves of ASS Li-S cell (1st cycle, green solid line; 2nd cycle, blue solid line). **b** Charge–discharge curves and rate performance of the ASS Li-S cell samples. **c** The specific capacities for sulfur during the discharge process. **d** Schematic of ASS Li-S cell.

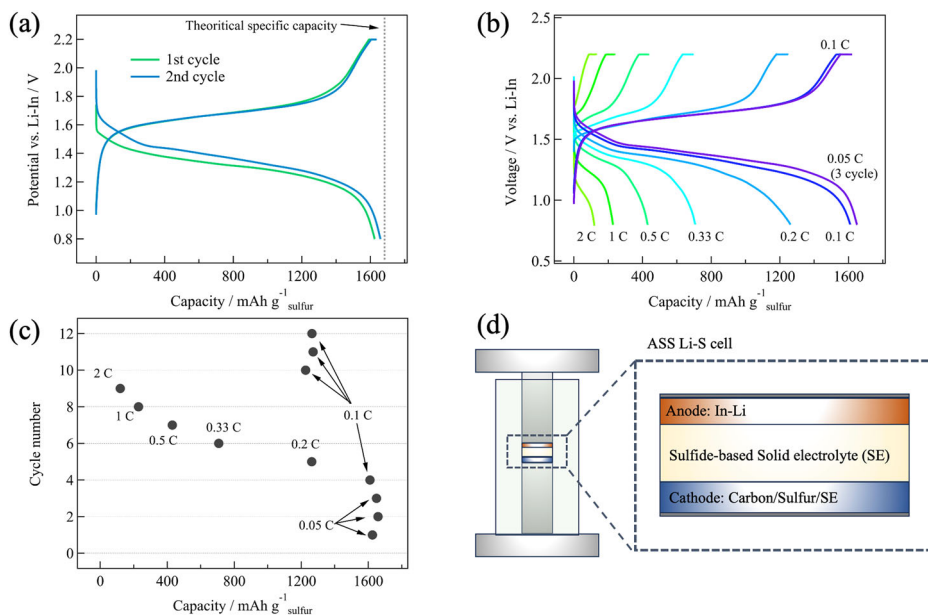


Table 1 | Samples

Num	Sample	C Wt%	S Wt%	SE Wt%	Surface area/ m ² /g ^a	Pore size 1/ nm, RSD ^b	Pore size 2/ nm, RSD ^b
1	CS_NoHeat	30	70	0	20	0.9, 45%	3.4, 35%
2	CS_Heat	30	70	0	8	0.5, 16%	4.3, 32%
3	CS_heat-SE	15	35	50	-	-	-
4	Carbon (cf.)	100	0	0	2840	0.7, 66%	3.7, 66%
5	Sulfur (cf.)	0	100	0	-	-	-

^aMeasured by N₂ adsorption at -196 °C using the BET method from desorption data.

^bMeasured by small-angle X-ray scattering (SAXS) using curve fitting.

electrolytes eliminate liquid leakage concerns and substantially reduce fire risks. Specifically, sulfide-based solid electrolytes (SEs) exhibit a conductivity comparable to liquid electrolyte systems, a wide operating temperature range, and good compatibility with sulfur^{41–43}. In addition, sulfur, as a cathode material, offers high theoretical capacity. It is lightweight^{44,45}, free of rare metals, abundant, and eco-friendly, making it suitable for high-performance and sustainable next-generation batteries¹.

The major challenges faced by ASS Li-S batteries include the low electronic conductivity of sulfur (or Li₂S) and the sluggish nature of redox reactions. Researchers have investigated various techniques, such as the formation of composites with carbon or metals^{16,46,47}, to address these challenges. A particularly effective technique involves the impregnation of sulfur into carbon pores via melt diffusion^{48–50}. This technique enhances battery performance by creating an optimal reaction environment for Li and electrons as well as increasing the contact area. For instance, Ando et al.⁵¹ reported a specific capacity of 1488 mAh g⁻¹ (89% of the theoretical specific capacity of sulfur) for ASS Li-S batteries prepared using melt diffusion-based composite formation of sulfur and porous carbon. This underscores the significance of forming a composite of amorphous sulfur and porous carbon. Hakari et al.⁵² achieved a specific capacity of 1100 mAh g⁻¹ per Li₂S (95% of the theoretical specific capacity) by doping Li-S with lithium halides to enhance its reactivity in electrochemical reactions. They also maintained a specific capacity of 980 mAh g⁻¹ (after 2000 cycles at 2 C), surpassing the performance of both conventional liquid-state and ASS Li-S batteries in terms of specific capacity and cycle life. Understanding the factors contributing to high-performance batteries and analyzing the structural changes before and after composite formation and charge–discharge cycles is essential for advancing the development of materials suitable for real-world applications.

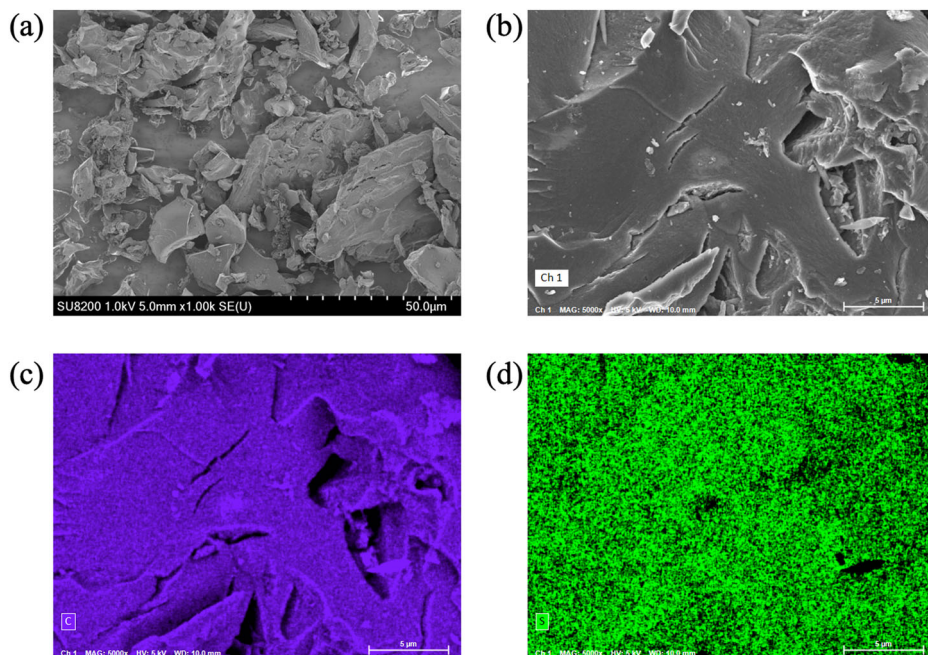
The analysis of sulfur reactions in electrode materials poses a substantial challenge in liquid-state and ASS systems. When sulfur is crystalline, it can be effectively evaluated using techniques such as in situ X-ray diffraction (XRD)^{46,53}. However, the structure becomes unknown when sulfur becomes amorphous due to composite formation^{51,54} or when the reaction intermediate Li₂S_x is amorphous. Consequently, spectroscopic approaches have been actively employed. For example, in situ Raman spectroscopy^{55–57}, X-ray absorption spectroscopy^{55,58}, and X-ray photoelectron spectroscopy⁵⁹ have been used to estimate the transformation from S₈ to Li₂S. In addition, the local structure of amorphous sulfur can vary depending on the carbon material. For instance, sulfur can exist as S₂ in nanopores⁵⁴ or S_n chains can be observed by transmission electron microscopy in carbon nanotubes⁶⁰. More direct methods for determining the structure of amorphous sulfur are required. In this study, we elucidated the local structure of sulfur in carbon pores using pair distribution function (PDF) analysis, which is suitable for both crystalline and amorphous phases.

Results and discussion

Charge–discharge results of ASS Li-S cell

Figure 1a shows the first and second charge–discharge curves of the ASS Li-S cell samples. The specific capacity for sulfur was 1625 and 1658 mAh g⁻¹ during the discharge process of the first and second cycles, respectively. These values validate the theoretical specific capacity and replicate the findings of a previous study⁵¹. This remarkable performance is attributed to the extensive contact area created between the sulfur-based SE, sulfur, and carbon with a large specific surface area (Table 1), as well as the effective formation of lithium-ion and electron transport pathways using a sulfur-based SE with excellent processability. The specific capacity for cathode of the ASS Li-S cell was 570 mAh g⁻¹.

Fig. 2 | SEM image and EDX mappings of CS_Heat. **a** $\times 1000$, **b** $\times 5000$, **c** C mapping, **d** S mapping.



The rate performance is shown in Fig. 1b, c. The ASS Li-S cell shows the capacity of 1649, 1610, 1262, 707, 430, 228, and 119 mAh g^{-1} at 0.05, 0.1, 0.2, 0.33, 0.5, 1, and 2 C, respectively. For 10th cycle, the capacity was 1226 mAh g^{-1} at 0.1 C. The observed decrease in capacity is attributed to charge transfer and diffusion resistance. Further improvements in rate characteristics are anticipated through the enhancement of the electronic conductivity of the cathode and the lithium-ion conductivity.

Sulfur impregnated

SEM-EDS was conducted to examine the dispersion of sulfur in the carbon-sulfur composite. The SEM-EDS result of CS_Heat was shown in Fig. 2. The distribution of C (Fig. 2c) and S (Fig. 2d) is consistent, confirming that S is not localized.

The BET-specific surface area was evaluated to assess the detailed state of carbon pores in ASS Li-S cells, which achieved a specific capacity per weight of sulfur close to the theoretical specific capacity. The specific surface area of Carbon (cf.) alone was 2840 m^2/g , while CS_NoHeat and CS_Heat decreased to 20 and 8 m^2/g , respectively, irrespective of the implementation of melt diffusion (Table 1). This decrease is attributed to sulfur adhering to the surface of carbon particles and obstructing the pore entrances, raising concerns about the accuracy of BET-specific surface area measurements for capturing the pore situation inside carbon materials.

SAXS measurements were performed to nondestructively evaluate the internal pore state of carbon particles. The results are shown in Fig. 3. Based on wide-angle X-ray scattering (WAXS), scattering below and above $5.0 \times 10^{-2} \text{ \AA}^{-1}$ primarily originated from particle scattering and pores, respectively⁶¹. CS_Heat, subjected to melt diffusion, exhibited a reduction in the shoulder between 5.0×10^{-2} and $0.5 \times 10^{-1} \text{ \AA}^{-1}$, indicating sulfur infiltration into pores. Notably, differentiating between nanopore scattering and WAXS was challenging. However, the scattering intensity ratio (the proportion of scattering intensity other than dummy scattering) from pores was 74.3%, 31.7%, and 4.2% for Carbon (cf.), CS_NoHeat, and CS_Heat, respectively (Fig. S1, Table S1). The primary factors affecting carbon and CS_NoHeat were a decrease in the contribution from carbon pores due to sulfur content and changes in the pore quantity and shape due to tumbling mill processing. The significant difference between CS_NoHeat and CS_Heat was the marked decrease in scattering intensity due to sulfur infiltrating the carbon pores via melt diffusion, resulting in a smaller density difference. The 4.2% scattering intensity for CS_Heat indicates remaining pores, attributable to the density difference between the carbon and sulfur

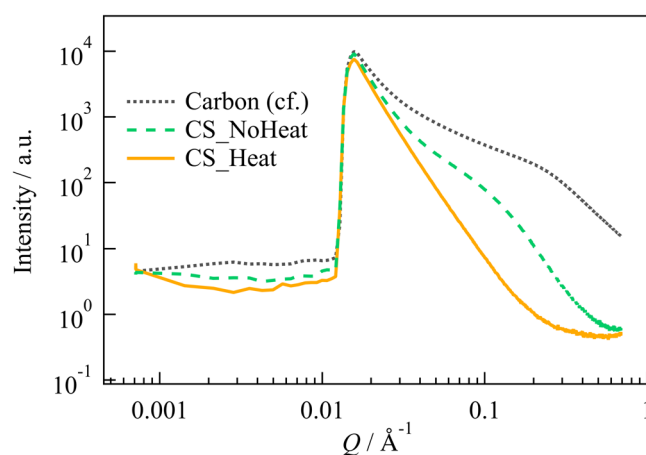


Fig. 3 | SAXS curves. Dotted line, carbon; dashed line, CS_NoHeat; and yellow solid line, CS_Heat.

materials. The quantitative analysis can be enhanced by refining the analysis model.

Regarding the carbon pore state of carbon-sulfur composites, BET evaluation is challenging because sulfur attaches to the carbon material surface and conventional morphology observation was limited to local observations⁴⁷. However, SAXS enabled the quantification of sulfur infiltration into carbon pores, offering a novel method.

Local structure of sulfur in carbon pores

Based on the results of 3–2, sulfur exists within the carbon pores. XRD measurements were conducted to confirm the sulfur structure (Fig. 4). CS_Heat was verified to be amorphous because no crystalline Bragg peaks were observed. This finding is consistent with those of previous studies^{49,51,56}.

To investigate the thermal behavior, thermogravimetric-differential thermal analysis (TG-DTA) was performed on Sulfur (cf.) and CS_Heat (Fig. 5). The phase transition peaks of sulfur (109 °C, 122 °C, 183 °C)⁶² were not observed in CS_Heat (Fig. 5a). This indicates that sulfur exists in an amorphous state within the carbon pores or is adsorbed on the surface of carbon particles (consistent with XRD patterns in Fig. 4), and the structure remains intact until the onset of vaporization at ~ 200 °C (Fig. 5b). The

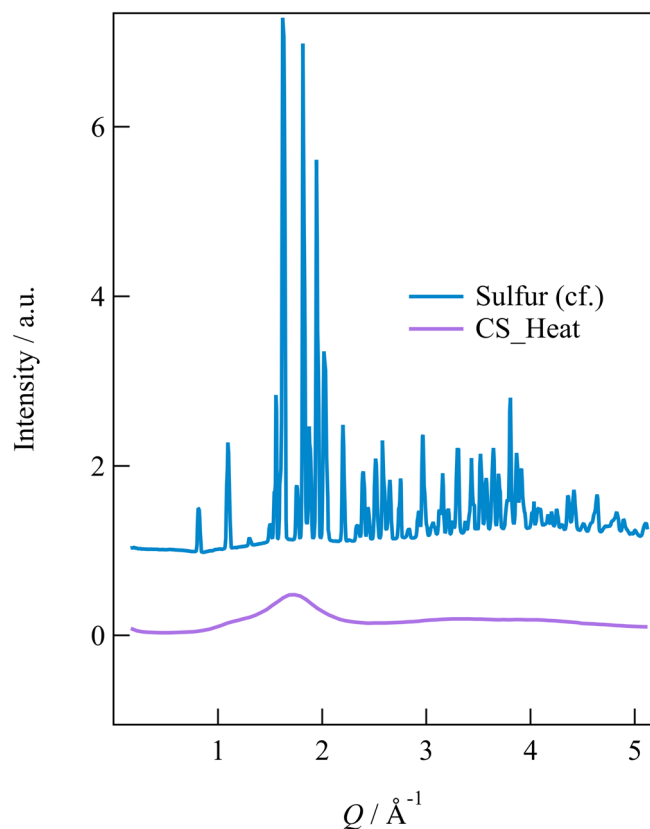


Fig. 4 | XRD patterns. Blue solid line, sulfur (cf.); purple solid line, CS_Heat.

completion temperature of sulfur vaporization, as indicated by the TG-DTA curve, increased from ~320 °C in Sulfur (cf.) to 460 °C in CS_Heat (Fig. 5b). This finding corroborates a previous study⁵¹ and signifies the influence of sulfur adsorption on the carbon walls in the samples. In addition, the C:S ratio calculated from the weight loss ratio was ~29:71, close to the initial ratio.

Based on the findings, we confirmed that sulfur infiltrates carbon pores and remains in an amorphous phase through melt diffusion.

The chemical state of Sulfur in CS_Heat was confirmed by XPS. Figure 6 presents the normalized S 2p peaks which split to S 2p_{3/2} (164.1 eV) and S 2p_{1/2} (165.3 eV) dual peaks with an area ratio ~2:1 causing by spin-orbit splitting⁵⁵. The lone dual peaks at high binding energies (169 eV) are attributed to the sulfonate⁶³. Compared to Sulfur(cf.), CS_Heat exhibited enhanced intensity for the S 2p_{1/2} and sulfonate peaks. This enhancement is attributed to variations in the conformation of sulfur or interactions with the carbon surface.

Figure 7 shows the PDF patterns of Sulfur (cf.), CS_Heat, and Carbon (cf.). Sulfur (cf.) exhibited peaks at 2.1, 3.4, and 4.5 Å, indicating intramolecular correlations stemming from the S₈ ring-shaped molecules⁶⁴. Peaks were also observed at 4.0, 5.5, 7.2, and 8.4 Å, representing intermolecular correlations derived from the crystalline structures. Meanwhile, CS_Heat exhibited peaks at 2.1, 3.4, and 4.5 Å, similar to those of Sulfur (cf.), indicating the presence of S₈ ring-shaped molecular structures. However, no distinct correlation peaks were noted beyond 5.0 Å, implying that the molecular size is under 5.0 Å. This observation is consistent with the overlap of the peaks at 2.1, 3.4, and 4.5 Å with those of Sulfur (cf.). The presence of S₈ was further confirmed through thermal decomposition GC-MS, which detected a peak corresponding to S₈ (Fig. S2).

Besides, CS_Heat exhibited peaks at 1.4, 2.5, and 2.8 Å, identified as in-plane correlations of graphene, and a peak at 3.8 Å, recognized as inter-plane correlations of graphene. These findings were based on Carbon (cf.) measurements and corroborated by previous studies⁶⁵. The absence of graphite correlation peaks beyond 4.0 Å is attributable to the lower

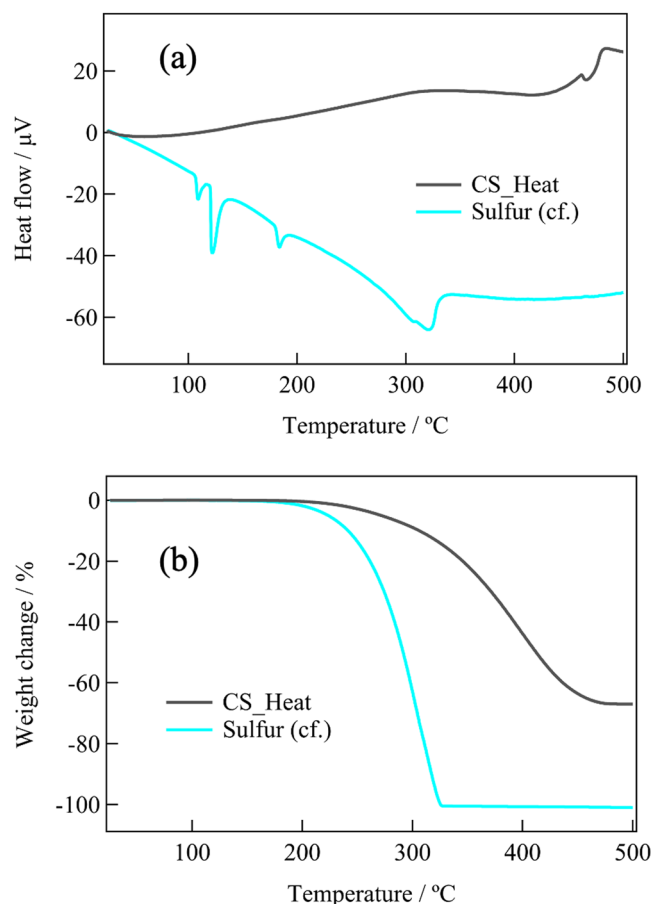


Fig. 5 | Thermal behaviors. a DTA. b TG: light blue solid line, Sulfur (cf.); Black solid line, CS_Heat.

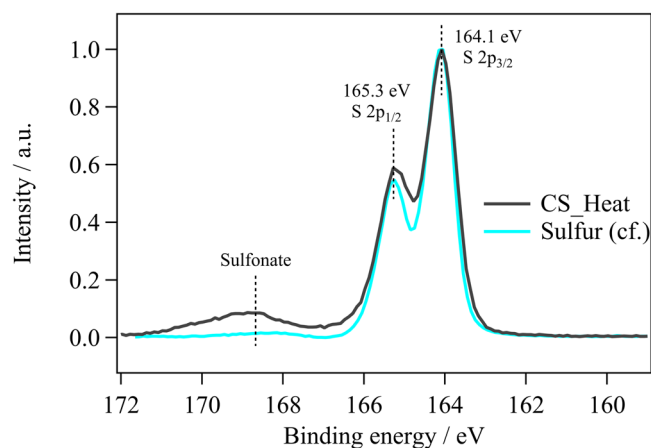


Fig. 6 | Chemical state of sulfur. XPS spectra of S 2p: Light blue solid line, Sulfur (cf.); Black solid line, CS_Heat. PDF analysis was conducted to comprehensively investigate the local structure of sulfur within the carbon pores.

scattering ability of carbon than sulfur and the challenge of detecting long-range correlation peaks due to the amorphous nature of carbon.

To explore possibilities beyond the proposed S₈ ring-shaped molecules in Sulfur (cf.), theoretical calculations were performed by applying the Gaussian method to the S₈ ring-shaped model, linear model, and linear model with intermolecular correlations. A comparison between the PDFs and the experimental PDF data (Fig. 7: yellow solid line) as total correlation functions, $T(r) = G(r) + 4\pi r\rho_0$ where ρ_0 is the number density, is presented in Fig. 8. The results for the S₈ monomolecular structure (ring model 1)

agreed with the experimental data (SC_Heat). The open-ring model 1 and 2 exhibited peaks at 6.2 and 5.7 Å, respectively, and did not match the experimental data. In addition, a crown-shaped S₈ ring model (ring model 2) showed a peak at 4.8 Å, which did not match the experimental data. Given the heat treatment, this indicates that the sulfur in the carbon pores has an S₈ ring-shaped structure (Fig. 9). The temperature for melt diffusion is 300 °C, a temperature at which sulfur can become a rubber-like linear form. Interactions with the carbon walls likely maintain the presence of the S₈ ring-shaped structure. Although the S₈ ring-shaped structure was the predominant average molecular structure in this study, the pore size and the type of carbon may result in different molecular structures⁵⁸.

Conclusions

We fabricated an ASS Li-S cell using a carbon–sulfur composite obtained via melt diffusion. We confirmed that the specific capacity per sulfur weight is close to the theoretical specific capacity. The presence of sulfur in carbon pores in the carbon–sulfur composite (CS_Heat) was quantitatively demonstrated by SAXS, supporting the concept of melt diffusion. SAXS provides an alternative or complementary evaluation to techniques such as BET and local evaluations for particles with blocked entrances, contributing to material design optimization by confirming the material quality. The sulfur in the carbon pores was directly evaluated as amorphous S₈ through PDF analysis and thermal decomposition GC–MS. This provides fundamental and crucial structural information for theoretical calculations and serves as primary data for understanding the structure of amorphous sulfur in different

composition techniques (such as solvent impregnation) and carbon materials with varying properties (such as carbon nanotubes and highly amorphous carbon materials). Further, this method has the potential for application development, such as controlling the pore size by varying the sulfur content and evaluating the resulting structure as well as assessing intermediate structures of amorphous sulfur during charge–discharge processes.

This study makes industrial and academical substantial contributions by accelerating the development and societal implementation of high-capacity and rare-metal-free next-generation ASS Li-S batteries. In addition, it directly and fundamentally elucidated the local structure.

Methods

Composite electrode preparation

The raw materials used were sulfur (S; FUJIFILM Wako Pure Chemical Corporation, 98.0%), porous carbon (MSC-30; Kansai Coke and Chemicals Co., Ltd.), and a Li₃PS₄-based sulfide SE (Idemitsu Kosan Co., Ltd.). MSC-30/S mixtures were prepared with a 3:7 weight ratio using a tumbling mill (CS_NoHeat). The estimated sulfur pore occupancy, based on the pore volume of the carbon material (1.58 ml/g) and the density of elemental sulfur (2.07 g/cm³), was 71.3%. This mixture was placed in a sealed stainless-steel container and heated at 150 °C for 6 h, followed by heating at ~300 °C for 3 h (CS_Heat). CS_Heat was then mixed with SE in a 1:1 weight ratio and 0.9 g of the mixture processed using a ZrO₂ pot (45 mL in volume) and 30 g of ZrO₂ balls (10 mm in diameter) with a planetary ball mill apparatus (Pulverisette 7, Fritsch) at 370 rpm for 20 h (CS_Heat-SE). All samples were prepared in an argon-filled glovebox. The prepared samples are listed in Table 1.

Cell assembly and electrochemical testing

CS_Heat-SE (5 mg) was loaded into a cylindrical mold made of Macor with a 10 mm diameter. Next, 100 mg sulfide-based SE (Idemitsu Kosan Co., Ltd.) was added and compressed to form the SE layer. Indium foil (thickness: 0.3 mm, diameter: 9.5 mm) and lithium foil (thickness: 0.2 mm, diameter: 9.5 mm) were subsequently added and compressed to form a three-layer structure comprising the cathode, SE layer, and anode. The three-layer pellet was then sandwiched between two stainless-steel disks as a current collector. Finally, an ASS Li-S cell (Fig. 1d) was obtained by cold-pressing.

Charge–discharge tests of the prepared ASS Li-S cells were conducted using a potentiostat and galvanostat (TOSCAT) from the Toyo System. The test voltage range was 0.8–2.2 V (vs. Li-In). Discharging was performed using the constant current (CC) method, whereas charging was performed using the constant current constant voltage (CCCV) method. The first and second cycles were charged and discharged at 0.146 mA/cm² (0.05 C) for the CC mode under room temperature (25 °C) and the cut off current for CV mode was set to 0.059 mA/cm² (0.02 C). For cycles 3 to 10, charging was performed at 0.1 C while discharging was conducted at varying rates. The capacity was calculated from the weight of sulfur.

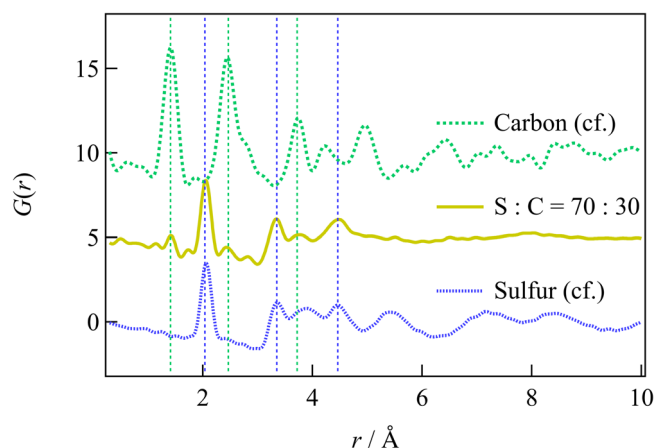


Fig. 7 | Differences in local structure. Comparison between the PDFs: upper dashed line, Carbon (cf.); yellow solid line, carbon–sulfur composites (CS_heat); lower dotted line, Sulfur (cf.).

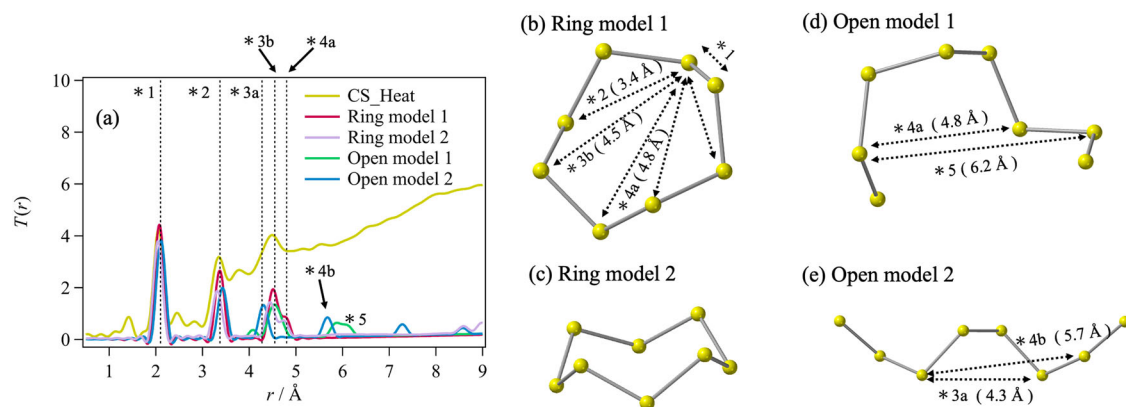


Fig. 8 | S₈ model structures calculated using the Gaussian method and their total correlation functions, $T(r)$. a comparison of $T(r)$ among these models and experimental data, b S₈ ring model 1, c S₈ ring model 2, d S₈ open-ring model 1, and e S₈ open-ring model 2.

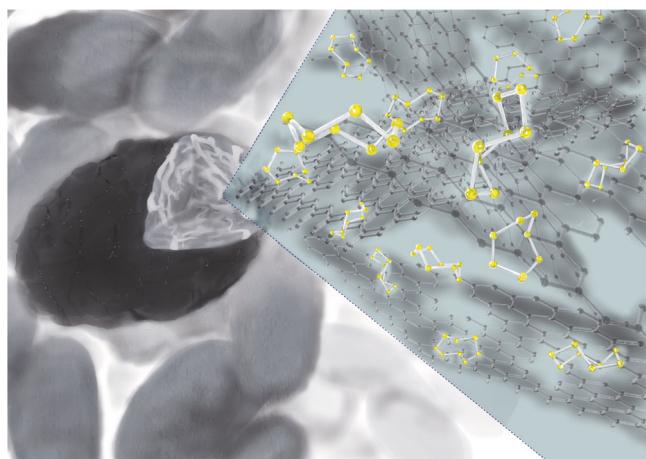


Fig. 9 | Image of carbon–sulfur composites. Sulfur forms the ring structure of S_8 , which is indicated in yellow atoms, within the gray-shaded carbon pores.

Characterization

Scanning electron microscopy (SEM) was performed using a field-emission scanning electron microscope (SU8220, HITACHI) equipped with an energy-dispersive X-ray spectroscopy system (X Flash5060FQ, Burker).

Specific surface area was determined using Autosorb-3 (Quantachrome), which employs the Brunauer–Emmett–Teller (BET) multipoint method based on nitrogen adsorption.

NANOPIX (Rigaku) was employed for small-angle X-ray scattering (SAXS) measurements. Cu K α radiation (wavelength approximately 1.54 Å) with a 40 kV voltage and 30 mA current served as the X-ray source. A 2-pinhole optical system was chosen for the incident beam. The camera length was approximately 598 mm, and the calibration was executed using the 1.513° peak of silver behenate. A HyPix-6000 2D semiconductor detector was used to perform a 12-frame measurement (5 min per frame, totaling 60 min) with a direct beam measurement of 10 s per frame (totaling 2 min). A 1/100 attenuator was employed during direct beam measurement. The samples were measured by sandwiching the powders between mending tapes. The 1D spectrum of SAXS was analyzed using SmartLab Studio II MRSAXS (Rigaku), and the scattering from the particle origin was fitted, assuming dummy scattering with a 300 nm diameter and a 40% normalized dispersion.

TG-DTA was performed using STA7200RV (Hitachi High-Tech). The mass was measured using a precise balance with ~10 mg samples placed in an open aluminum pan with a 5 mm height. The temperature was increased from 25 °C to 500 °C at a rate of 20 °C/min under N_2 flow at 200 ml/min.

Synchrotron-based total X-ray scattering measurements with PDF analysis were performed using the BL04B2 beamline in SPring-8, Japan, with an incident X-ray energy of 61.4 keV⁶⁶. The samples were hermetically sealed in a 2.0 mm Φ borosilicate glass capillary of 0.01 mm wall thickness within a glovebox under an argon atmosphere with a controlled dew point. The data were collected using Ge and CdTe hybrid detectors. The reduced PDF $G(r)$ was obtained via the conventional Fourier transform of the Faber–Ziman structure factor $S(Q)$ extracted from the collected data⁶⁷.

Structural optimization calculations were performed using the Gaussian method. The density functional theory calculations employed the B3LYP functional and cc-pVDZ basis set.

For the thermal decomposition gas chromatography–mass spectrometry (GC–MS) measurements, an EGA/Py-3030D thermal decomposition apparatus (Frontier Laboratories) and an 8890 GC/5977B MSD (Agilent Technologies) were used. The sample amount ranged from 130 to 170 μ g with temperature increase from 40 °C to 600 °C at a rate of 20 °C/min under a helium gas flow rate of 11 ml/min. The column used was an Ultra ALLOY with an inert deactivated tube (0.25 $\times$ 0.47 mm²). The weight ratio was 10:1, oven temperature of GC–MS was set to 300 °C, and ion source temperature was set to 300 °C. The m/z range extended up to 300.

X-ray photoelectron spectroscopy (XPS, VersaProbeII, ULVAC-PHI) using monochromatic Al K α radiation (100 W) at room temperature. Charge neutralization was required to minimize sample charging.

Data availability

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Author contributions

All authors contributed to the study conception and design. Material preparation was performed by H. Yamaguchi, Y.I., and Y.H. Data collection was performed by H. Yamaguchi, K.K., S.H., H. Yamada, J.T., S.S., and K.O. Data analysis were performed by H. Yamaguchi, Y.I., Y.H., A.S., A.H., K.K., S.H., H. Yamada, J.T., S.S., and K.O. The first draft of the manuscript was written by H. Yamaguchi and K.O. and all authors commented on the first version of the manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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